

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo6319/SBU-114

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

To be Assigned **09/807322**

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP99/07691

13 October 1999 (13.10.99)

26 October 1998 (26.10.98)

TITLE OF INVENTION METHOD OF PREPARING RIGID POLYURETHANE FOAM

APPLICANT(S) FOR DO/EO/US Takanori Chiba; Takuya Matsumoto; Keiichi Kitano

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

PTO Form 1449

U.S. APPLICATION NO. (if known) 09/807322 To be Assigned		INTERNATIONAL APPLICATION NO. PCT/EP99/07691		ATTORNEY'S DOCKET NUMBER Mo-6319/SBU-114	
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(l)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY <table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:50%; text-align: right;">\$</td> <td style="width:50%; text-align: center;">860.00</td> </tr> <tr> <td style="text-align: right;">\$</td> <td></td> </tr> </table>		\$	860.00	\$	
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Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:50%; text-align: right;">\$</td> <td style="width:50%;"></td> </tr> </table>		\$			
\$									
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE						
Total claims	10 -20 =	0	x \$18.00	\$	0.00				
Independent claims	2 -3 =	0	x \$80.00	\$	0.00				
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	0.00				
TOTAL OF ABOVE CALCULATIONS =				\$	860.00				
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0.00				
SUBTOTAL =				\$	860.00				
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$					
TOTAL NATIONAL FEE =				\$	860.00				
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	0.00				
TOTAL FEES ENCLOSED =				\$	860.00				
				Amount to be refunded:	\$				
				charged:	\$				

a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 860.00 to cover the above fees.
 A duplicate copy of this sheet is enclosed.


c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.


d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Lyndanne M. Whalen
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00157
 PATENT TRADEMARK OFFICE


 SIGNATURE
Lyndanne M. Whalen
 NAME
29,457
 REGISTRATION NUMBER

09/807322

JC02 Rec'd PCT/PTO 11 APR 2001

PATENT APPLICATION
Mo-6319
SBU-114

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
TAKANORI CHIBA ET AL) PCT/EP 99/07691:
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: METHOD OF PREPARING)
RIGID POLYURETHANE FOAM)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

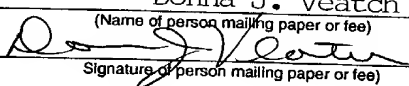
Upon granting the enclosed application a Serial Number and filing date,
please amend this application as follows:

"Express Mail" mailing label number EK633383539US
Date of Deposit April 11, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee)

IN THE CLAIMS:

Please Cancel Claims 1-4.

Please add the following New Claims 5-14:

- - 5. A process for preparing a rigid polyurethane foam comprising reacting
 - a) an organic polyisocyanate with
 - b) an isocyanate-reactive composition comprising
 - (i) a polyether polyol and/or a polyester polyol having poor compatibility with cyclopentane,
 - (ii) cyclopentane,
 - (iii) water,
 - (iv) a surfactant, and
 - (v) a catalyst
 in which the cyclopentane is dispersed in the isocyanate-reactive composition.
- 6. The process of Claim 5 in which the cyclopentane is dispersed in a high pressure circulating line equipped with a static mixer.
- 7. The process of Claim 5 in which a polyether polyol is employed.
- 8. The process of Claim 7 in which the polyether polyol is the addition polymerization product of an initiator, ethylene oxide and propylene oxide.
- 9. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 20 g in 100 g of polyol.
- 10. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 10 g in 100 g of polyol.
- 11. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 5 g in 100 g of polyol.

12. An apparatus useful for dispersing cyclopentane in an isocyanate-reactive mixture which includes a polyol having poor compatibility with cyclopentane comprising a polyol tank, a static mixer and a high pressure circulating line in which the static mixer is in the high pressure circulating line.
13. The apparatus of Claim 12 in which the polyol tank is equipped with a stirrer.
14. The apparatus of Claim 13 in which the stirrer is operated at a circumferential speed of at least 0.5 m/s. - -

Please add the following Abstract to the specification:

- - Rigid polyurethane foams are made by reacting an organic polyisocyanate with a polyol component that includes a polyether and/or polyester polyol, water and a cyclopentane blowing agent. The polyether polyol and/or polyester polyol employed is characterized by poor compatibility with cyclopentane. The cyclopentane is dispersed in the polyol component before that polyol component is reacted with the polyisocyanate. An apparatus for dispersing cyclopentane in the polyol component is also disclosed.- -

REMARKS

Claims 1-4 have been cancelled and rewritten as new Claims 5, 6, 7, 8, and 12-14 to place them in a more commonly used form. New Claims 9-11 have been added to specifically claim preferred embodiments of the invention.

New Claim 5 corresponds to original Claim 1.

New Claim 6 corresponds to original Claim 2.

New Claims 7 and 8 are directed to the subject matter of original Claim 3.

New Claims 9-11 specifically recite solubilities for the cyclopentane in the polyol. Support for these claims is found at page 3, lines 1-4 of the specification.

New Claims 12-14 are directed to the subject matter of original Claim 4.

An Abstract of the Disclosure has been added. A copy of new page 16 containing the Abstract is enclosed.

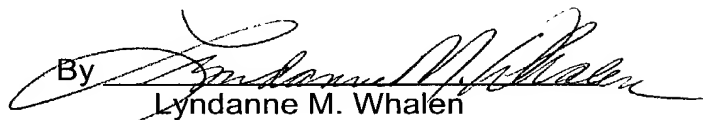
Attachment A on which the changes made herein are summarized is enclosed.

An action on the merits of this case is respectfully requested.

Respectfully submitted,

TAKANORI CHIBA
TAKUYA MATSUMOTO
KEIICHI KITANO

By



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ATTACHMENT A

Claims 1-4 have been cancelled.

The following new claims have been added.

5. A process for preparing a rigid polyurethane foam comprising reacting
 - c) an organic polyisocyanate with
 - d) an isocyanate-reactive composition comprising
 - (vi) a polyether polyol and/or a polyester polyol having poor compatibility with cyclopentane,
 - (vii) cyclopentane,
 - (viii) water,
 - (ix) a surfactant, and
 - (x) a catalystin which the cyclopentane is dispersed in the isocyanate-reactive composition.
6. The process of Claim 5 in which the cyclopentane is dispersed in a high pressure circulating line equipped with a static mixer.
7. The process of Claim 5 in which a polyether polyol is employed.
8. The process of Claim 7 in which the polyether polyol is the addition polymerization product of an initiator, ethylene oxide and propylene oxide.
9. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 20 g in 100 g of polyol.
10. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 10 g in 100 g of polyol.
11. The process of Claim 5 in which the solubility of cyclopentane in the polyol is less than or equal to 5 g in 100 g of polyol.

12. An apparatus useful for dispersing cyclopentane in an isocyanate-reactive mixture which includes a polyol having poor compatibility with cyclopentane comprising a polyol tank, a static mixer and a high pressure circulating line in which the static mixer is in the high pressure circulating line.

13. The apparatus of Claim 12 in which the polyol tank is equipped with a stirrer.

14. The apparatus of Claim 13 in which the stirrer is operated at a circumferential speed of at least 0.5 m/s..

The following new Abstract has been added:

Rigid polyurethane foams are made by reacting an organic polyisocyanate with a polyol component that includes a polyether and/or polyester polyol, water and a cyclopentane blowing agent. The polyether polyol and/or polyester polyol employed is characterized by poor compatibility with cyclopentane. The cyclopentane is dispersed in the polyol component before that polyol component is reacted with the polyisocyanate. An apparatus for dispersing cyclopentane in the polyol component is also disclosed.

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-16-

METHOD FOR PREPARING RIGID POLYURETHANE FOAM

ABSTRACT OF THE DISCLOSURE

Rigid polyurethane foams are made by reacting an organic polyisocyanate with a polyol component that includes a polyether and/or polyester polyol, water and a cyclopentane blowing agent. The polyether polyol and/or polyester polyol employed is characterized by poor compatibility with cyclopentane. The cyclopentane is dispersed in the polyol component before that polyol component is reacted with the polyisocyanate. An apparatus for dispersing cyclopentane in the polyol component is also disclosed.

Mo-6319

WO 00/24813

PCT/EP99/07691

Method of preparing rigid polyurethane foam

5 The present invention relates to a method of preparing a rigid polyurethane foam and an apparatus for preparing a rigid polyurethane foam. The rigid polyurethane foam can be used as heat insulation materials for freezer, refrigerator, building and the like.

10 Rigid polyurethane foams are widely used as heat insulation materials for refrigerator-freezer, for example, refrigerators for household use, since they have a low product density, excellent heat insulating properties and a high mechanical strength.

15 As blowing agents for preparing the rigid polyurethane foams, chlorofluorocarbons (hereinafter referred to as CFCs), in particular trichlorofluoromethane (CFC-11), have been conventionally used.

20 However, since the CFC-11 blowing agent contains halogens, there is apprehension that it may deplete the ozone layer and cause the environmental issues such as global warming. For the purpose of protecting the global environment, the amounts of production and consumption of CFCs are now under international regulations. In Japan, the production of CFCs had been prohibited by the end of 1995. As substitute new blowing agents, hydrochlorofluorocarbons (HCFCs) having a low ozone depletion potential are used. For example, HCFC-141b (1,1-dichloro-1-fluoroethane), HCFC-22 (chlorodifluoromethane), HCFC-142b (1-chloro-1,1-difluoroethane) have been introduced and applied as blowing agents.

However, use of HCFCs, the substitute for CFCs, are now phased down, because they also contain chlorine atom in their molecules and therefore still retain the property of depleting the ozone layer although their effects on the ozone layer are little. Thus, in terms of global environmental protection, use of blowing agents having no effects on the ozone layer depletion at all was newly proposed. Hydrocarbon-based blowing agents which contain no chlorine atom and pose no risk

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Donna J. Veatch

(Name of person mailing paper or fee)

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of depleting the ozone layer, for example cyclopentane, have already been introduced and applied for some purposes.

5 However, although cyclopentane is most suitable as an earth-friendly blowing agent, it involves some drawbacks. In particular, gaseous cyclopentane itself has a high thermal conductivity and the heat insulating performance of the rigid polyurethane foams employing cyclopentane is therefore inferior to those employing conventional HCFC-141b. Accordingly, there is a need for improving the heat insulation characteristics of such rigid polyurethane foams.

10

The present invention provides a method of preparing a rigid polyurethane foam from

- 15 (1) an organic polyisocyanate comprising an aromatic polyisocyanate,
- (2) a polyol comprising a polyether polyol and/or polyester polyol,
- (3) a blowing agent, and
- 20 (4) a surfactant, a catalyst and other auxiliaries,

characterized in that

25 the blowing agent (3) is cyclopentane and water,

25

the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane, and

30 cyclopentane is mixed and dispersed in a polyol premix comprising the components (2) to (4).

The phrase "having poor compatibility with cyclopentane" means that the solubility of cyclopentane in the polyol is 20 g or below, for example 10 g or below, and particularly 5 g or below. The term "solubility" means the number of grams of cyclopentane which are soluble in 100 g of the polyol at 25°C.

5

In order to mix and disperse cyclopentane in the polyol premix, it is preferred to use a stirrer of which circumferential speed is at least 5 m/s. In order to allow the dispersed liquid to exist stably in the tank of the foaming machine, it is preferred to stir the mixture at a circumferential speed of at least 0.5 m/s and circulate the mixture through a static mixer.

10

The present invention provides a composition for preparation of a rigid polyurethane foam, comprising

15

(1) an aromatic polyisocyanate,

(2) a polyether polyol and/or polyester polyol,

(3) a blowing agent comprising a mixture of cyclopentane and water, and

20

(4) a catalyst, a surfactant and other auxiliaries,

and further provides a method of preparing a rigid polyurethane foam from said composition by mechanically disperse cyclopentane in the polyol premix comprising the components (2), (3) and (4).

25

As the aromatic polyisocyanate (1), for example, polyisocyanates such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and polymethylene polyphenyl polyisocyanate (polymeric MDI), or modified polyisocyanates thereof can be used alone or in combination with each other.

30

Modified polyisocyanates, that is, products obtained by partial chemical reactions of organic di- and/or polyisocyanates may be used. For example, di- and/or polyisocyanates containing an ester, urea, biuret, allophanate, carbodiimide, isocyanurate and/or urethane group can be used.

5

The NCO content of the aromatic polyisocyanate (1) is preferably 30 to 50% by weight, for example, 30 to 33% by weight.

The polyol (2) is a polyether polyol and/or polyester polyol.

10

The polyether polyol may be obtained by addition polymerization of propylene oxide and/or ethylene oxide using a polyhydric alcohol such as ethylene glycol, propylene glycol, glycerine, trimethylolpropane, pentaerythritol, sorbitol, sucrose, or bisphenol A, an aliphatic amine such as triethanolamine or ethylenediamine, or an aromatic amine such as toluenediamine or methylenedianiline (MDA) as a starting material.

15

The polyether polyol may be obtained by a known method, for example, by anionic polymerization of an alkylene oxide using a starting material containing 2 to 8, preferably 3 to 8, reactive hydrogen atoms in its molecule, with using an alkali hydroxide such as potassium hydroxide or sodium hydroxide or an alkali alcoholate such as potassium methylate or sodium methylate as a catalyst. Alternatively, the polyether polyol may also be obtained by cationic polymerization of an alkylene oxide using a Lewis acid such as antimony pentachloride or boron fluoride etherate as a catalyst.

20

25

Suitable alkylene oxides are tetrahydrofuran, ethylene oxide, 1,3-propylene oxide, 1,2- or 2,3-butylene oxide, 1,2-propylene oxide, and styrene oxide. Ethylene oxide and 1,2-propylene oxide are particularly preferred. These alkylene oxides may be used alone or a mixture thereof.

30

As the diol, ethylene glycol, diethylene glycol, 1,2- or 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 1,10-decanediol may be

used, and glycerine or trimethylolpropane may be used as a triol. Similarly, lactone-based polyester polyols may also be used.

5 The polyester polyol preferably contains 2 to 3, especially preferably 2, functional groups, and those having a hydroxyl value of 200-600 mg KOH/g, preferably of 350-450 mg KOH/g, are suitable.

10 It is preferred that at least part of the polyol, in particular at least 10% by weight of the polyol, for example at least 30% by weight, is a polyether polyol prepared by addition polymerization of ethylene oxide and propylene oxide to an initiator such as sorbitol.

15 As the blowing agent (3), a combination of cyclopentane and water is used. The amount of water used herein is 0.1 to 5 parts by weight, preferably 0.1 to 1 part by weight, per 100 parts by weight of the polyol. The amount of cyclopentane is preferably 5 to 30 parts by weight, more preferably 10 to 25 parts by weight, per 100 parts by weight of the polyol.

20 As the catalyst, the surfactant and other auxiliaries, those conventionally known may be used. Amine catalysts or metal catalysts may be used as the catalyst.

25 As the amine catalyst, a tertiary amine such as triethylenediamine, tetramethylhexamethylenediamine, pentamethyldiethylenetriamine, or methylmorpholine can be used.

30 As the metal catalyst, an organic metal compound such as stannous octoate, dibutyltin dilaurate, or lead octylate can be used. The amount of the catalyst is preferably 0.01 to 5 parts by weight, more preferably 0.05 to 2.5 parts by weight, per 100 parts by weight of the polyol.

As the surfactant, usual organic silicone-based compounds may be used. For example, L6900, SZ-1684, SZ-1689 or the like manufactured by Nihon Unicar Company Limited, F395 or the like of Shin-Etsu Chemical Co., Ltd., or B8465, B8474 or the like available from Goldschmidt may be used. The amount of the surfactant is 0 to 5 parts by weight, preferably 0.5 to 3 parts by weight, per 100 parts by weight of the polyol.

In the present invention, other auxiliaries such as foaming stabilizers, foam controlling agents, fillers, dyes, pigments, flame retardant additives, anti-hydrolysis agents may be used in appropriate amounts.

For preparation of polyurethane foam, the polyisocyanate and the polyol premix are injected into a mold to harden using a high pressure foaming machine. The NCO index of the polyisocyanate and the polyol premix may be 90 to 150, for example, 110 to 130.

Preferably, the high pressure foaming machine has a circulating line (for example, a high pressure circulating line) and a polyol tank.

The polyol premix is a mixture prepared by adding cyclopentane to a mixture of the polyol, the surfactant, the catalyst, water as a blowing agent and other auxiliaries, and mechanically mixing and dispersing them.

Although the stirrer for mechanically stirring the polyol premix may be any of usual stirrers, those having a circumferential speed of at least 5 m/s is preferred.

For example, cyclopentane may be mechanically mixed and dispersed by a stirrer having stirring wings of 7 cm in diameter at 1700 rpm (circumferential speed: 6 m/s), and fed into the polyol tank of a cyclopentane-compatible high pressure foaming machine having a static mixer in the high pressure circulating line.

A commercially available static mixer is sufficient for this purpose, and for example, a 1 inch x 8 blocks static mixer available from SULZER Corporation may be used.

5 On the other hand, the polyol dispersion liquid can stably exist by reasons that the circumferential speed of the stirrer of the polyol tank is at least 0.5 m/s and the circulating line of the high pressure foaming machine contains the static mixer.

10 By using such high pressure foaming machine, rigid polyurethane foams may be prepared by a prepolymer process or a one-shot process using a batch method or a continuous method. One particularly preferred method is a method of processing conducted according to a two-components process (Component A: isocyanate, Component B: polyol premix).

15 Components A and B are mixed at a temperature in the range of 15 to 35°C, and injected into a mold thermoregulated at 20 to 60°C (for example, 35 to 45°C), and foamed to give a rigid polyurethane foam.

20 The rigid polyurethane foam may be used as heat insulation materials for freezer, refrigerator, building and the like.

The present invention is further demonstrated by the following Examples and Comparative Examples.

5

Cyclopentane Compatibility

Into a test tube, 100 g of a polyol is placed, a given amount of cyclopentane is added, and stirred and mixed thoroughly. After allowing to stand for one day, it is observed whether the mixture is clear, cloudy or separated. When the mixture is clear, the evaluation is "soluble". When the mixture is cloudy or separated, the evaluation is "insoluble".

10

Compression Strength

The measurement is conducted using a universal tester (TCM 1000 manufactured by Minebea Co., Ltd.) according to JIS-A-9514.

15

Core Foam Density

The core foam density refers to the density at the central part of the foam, and is calculated by measuring the weight down to 0.01 g and measuring the volume down to 0.1 cm³ by a water displacement method.

20

Thermal Conductivity

The measurement is conducted on a 200 mm × 200 mm × 25 mm sample cut from the core of the foam, using a thermal conductivity tester (Auto Lambda manufactured by EIKO Instruments Trading, Co.) according to ASTM-C-518.

25

Example 1

A polyol mixture liquid was prepared by adding an amine catalyst (1.8 parts by weight of tetramethylhexamethylenediamine plus 1.0 part by weight of pentamethyldiethylenetriamine plus 0.5 part by weight of trisdimethylaminopropyl-s-triazine), 2 parts by weight of a surfactant (L6900 manufactured by Nihon Unicar Company Limited), and 0.5 part by weight of water to 30 parts by weight of Polyol A, 25 parts by weight of Polyol B, 20 parts by weight of Polyol C, 20 parts by weight of Polyol D, and 10 parts by weight of Polyol E.

To the polyol mixture liquid, 21 parts by weight of cyclopentane (blowing agent), was added, and mechanically mixed and dispersed by a stirrer having 7-cm stirring wings at 2,000 revolutions/min (circumferential speed: 7 m/s) to prepare the final polyol mixture. The polyol mixture liquid was fed into a high pressure foaming machine equipped with a static mixer (a 1 inch x 8 blocks mixer manufactured by SULZER Corporation), and mixed by circulating it at high pressure for a while. The solubility of cyclopentane was 5 g or below per 100 g of the polyols.

According to the mixing ratio shown in Table 1, the polyol mixture and polymeric MDI were mixed and foamed. The urethane feedstocks were adjusted at the temperature of 20°C, and injected into a 600 mm x 400 mm x 50 mm aluminum mold adjusted at 45°C, and the molded product was demolded from the mold after 7 minutes. Physical properties of the molded product are shown in Table 1.

Examples 2 and 3

A polyol mixture liquid was prepared according to Table 1. As a silicone-containing surfactant, 2 parts by weight of F395 manufactured by Shin-Etsu Chemical Co., Ltd. was used. The other procedures were the same as those described in Example 1. Physical properties of the molded product are shown in Table 1.

Comparative Examples 1 and 2

As in Example 1, a polyol mixture liquid was prepared according to Table 1. The
5 mixture liquid was then mixed with cyclopentane, and fed into the high pressure
foaming machine, and the molded product was obtained in the same manner as in
Example 1. The difference between these Comparative Examples and Examples 1-3
is in that the polyol mixture liquid in these Comparative Examples was a liquid in
which cyclopentane was completely dissolved. Physical properties of the molded
10 product are shown in Table 1.

Polyol A:

A polyol obtained by addition of EO (ethylene oxide) and PO (propylene oxide) to
sorbitol as a starting material, having a hydroxyl value of 550 mg KOH/g

15

Polyol B:

A polyol obtained by addition of PO to glycerin as a starting material, having a
hydroxyl value of 520 mg KOH/g

20

Polyol C:

A polyol obtained by addition of EO to trimethylolpropane as a starting material,
having a hydroxyl value of 550 mg KOH/g

Polyol D:

25 A polyol obtained by addition of PO to trimethylolpropane as a starting material,
having a hydroxyl value of 865 mg KOH/g

Polyol E:

30 A polyester polyol derived from polyethylene terephthalate, having a hydroxyl value
of 315 mg KOH/g

Polyol F:

A polyol obtained by addition of EO to ethylene glycol as a starting material, having a hydroxyl value of 374 mg KOH/g

5 Polyol G:

A polyester polyol derived from phthalic acid and diethylene glycol, having a hydroxyl value of 420 mg KOH/g

Polyol H:

10 Glycerin

Polyol J:

A polyol obtained by addition of PO to glycerin as a starting material, having a hydroxyl value of 390 mg KOH/g

15

Polyol K:

A polyol obtained by addition of PO to toluenediamine/diethanolamine as starting materials, having a hydroxyl value of 450 mg KOH/g

20 Polyol L:

A polyol obtained by addition of PO to sugar/propylene glycol as starting materials, having a hydroxyl value of 380 mg KOH/g

Polyol M:

25 A polyol obtained by addition of PO to propylene glycol as a starting material,
having a hydroxyl value of 500 mg KOH/g

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Polyol A	30	35	30	-	-
Polyol B	25	-	25	-	-
Polyol C	25	-	-	-	-
Polyol D	10	-	-	-	-
Polyol E	10	-	-	-	-
Polyol F	-	20	20	-	-
Polyol G	-	20	20	15	-
Polyol H	-	5	5	-	-
Polyol J	-	20	-	-	-
Polyol K	-	-	-	40	50
Polyol L	-	-	-	45	40
Polyol M	-	-	-	-	10
Cyclopentane	21	21.5	21.5	15.5	11.2
water	0.5	0.5	0.6	1.3	2.0
Polymeric MDI	170	130	130	123	140
Compressive strength (kg/cm ²)	2.0	1.5	1.6	1.5	2.0
Core foam density (kg/m ³)	35	32	32	32	35
Thermal conductivity × 10 ⁻⁴ (kcal/mh°C)					
25°C	163	161	162	163	173
10°C	154	155	156	158	168
0°C	150	151	152	156	166
Pentane compatibility (solubility: g)	Insoluble, ≤5 g	Insoluble, ≤5 g	Insoluble, ≤5 g	Soluble	Soluble

- 5 According to the present invention, a rigid polyurethane foam having a low thermal conductivity and excellent heat insulating properties can be prepared by using polyols having poor compatibility with cyclopentane.

30 4. An apparatus for preparing a rigid polyurethane foam, used in the method of claim 1, characterized in that it comprises a static mixer in a high pressure

circulating line for mixing and dispersing cyclopentane, and the circumferential speed of a stirrer of a polyol tank is at least 0.5 m/s.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08J 9/14, B29C 44/34, C08J 9/30 // C08L 75/04	A1	(11) International Publication Number: WO 00/24813 (43) International Publication Date: 4 May 2000 (04.05.00)
(21) International Application Number: PCT/EP99/07691 (22) International Filing Date: 13 October 1999 (13.10.99) (30) Priority Data: 10-303794 26 October 1998 (26.10.98) JP (71) Applicant (for all designated States except US): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): CHIBA, Takanori [JP/JP]; 11-16, Shinkofudai 5-chome, Toyono-cho, Toyono-gun, Osaka 563-0105 (JP). MATSUMOTO, Takuya [JP/JP]; 25-18, Motomachi, Suita, Osaka 564-0031 (JP). KITANO, Keiichi [JP/SG]; 53 Jurong East Avenue 1, #09-06, Pare Oasis 609783, Singapore (SG). (74) Common Representative: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD OF PREPARING RIGID POLYURETHANE FOAM		
(57) Abstract <p>A method of preparing a polyurethane foam having excellent heat insulating properties is provided. A method of preparing a rigid polyurethane foam from (1) an organic polyisocyanate comprising an aromatic polyisocyanate, (2) a polyol comprising a polyether polyol and/or polyester polyol, (3) a blowing agent, and (4) a surfactant, a catalyst and other auxiliaries, characterized in that the blowing agent (3) is cyclopentane and water, the polyol (2) is a polyether polyol and/or polyester polyol having poor compatibility with cyclopentane, and cyclopentane is mixed and dispersed in a polyol premix comprising the components (2) to (4).</p>		

COMBINED DECLARATION AND POWER OF ATTORNEY

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

"METHOD OF PREPARING RIGID POLYURETHANE FOAM"

the specification of which is attached hereto,

or was filed on **October 13, 1999**

as a PCT Application Serial No. **PCT/EP99/07691**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

10-303794
(Number)

Japan
(Country)

October 26, 1998
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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